of this suggestion from the status of a working hypothesis to that of a mechanistic proposal.

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Synthesis and Structural Characterization of Three New Platinum(IV) Halide Anions as Triphenylcarbenium[1] Salts. Isolation from Reaction of Platinum Tetrachloride with Trityl Chloride in Benzene of a Novel $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ Anion Containing *o*-Phenylene Ligands[2]

Sir:

We wish to report the preparation and characterization of $[(C_6H_5)_3C]^+[PtCl_5 \cdot CH_2Cl_2]^-$ (**1**), $[(C_6H_5)_3C]^+{}_2[Pt_2Cl_{10}]^{2-}$ (**2**), $[(C_6H_5)_3C]^+{}_2[Pt_3Cl_{12}]^{2-}$ (**3**), $[(C_6H_5)_3C]^+{}_2[Pt_3Cl_{12}]^{2-} \cdot 2C_2H_2Cl_4$ (**4**), and $[(C_6H_5)_3C]^+{}_2[Pt_4(C_6H_4)_2Cl_{14}]^{2-} \cdot 2CH_2Cl_2$ (**5**) by the previously unreported reaction of $[PtCl_4]_4$[3] with $(C_6H_5)_3CCl$ in various solvents (including methylene chloride and benzene). The three polymeric platinum halide anions of **2**–**5** are hitherto unknown for platinum and its congeners (palladium and nickel); furthermore, the anion of **3** and **4** represents a rare example of a compound possessing metal atoms with mixed valency (*viz.*, Pt(II) and Pt(IV) within the same discrete unit), while the novel anion of **5** provides the first case determined by X-ray diffraction of a substituted benzene ring σ bonded to more than one transition metal atom. This communication thereby illustrates the possible diversity and scope of the general reaction of anhydrous transition metal chlorides with triphenylmethyl chloride under varying conditions to give new anions of unusual stoichiometry.

Our study of the reactions of $[PtCl_4]_4$ with $(C_6H_5)_3CCl$ was predicated on the basis that the well-known $[PtCl_6]^{2-}$ anion may not be produced due to the inability of a $[PtCl_5]^-$ species to ionize $(C_6H_5)_3CCl$ further. Since Pt(IV) invariably possesses an octahedral-like coordination, one may expect dimerization of $[PtCl_5]^-$ to give the previously unknown $[Pt_2Cl_{10}]^{2-}$ anion.

The coordinating ability of the solvent used for the reaction of $[PtCl_4]_4$ with $(C_6H_5)_3CCl$ appears to determine the nature and extent of the products isolated. A finely powdered slurry of $[PtCl_4]_4$ in CH_2Cl_2 reacts completely under nitrogen with $(C_6H_5)_3Cl$ in slight excess of 1:1 mole ratio to give an orange solution which yields yellow-orange crystals of **1** upon evaporation of solvent. A few deep red crystals of **2** and orange-red crystals of **3** invariably crystallize out with **1**. Slow evaporation of solvent from the red solution, which results from the above orange solution standing for 48 hr or more, gives some crystals of **1** with increased amounts of **2** and **3**. Although the yields of **2** and **3** vary from 5 to 20 and 10 to 40%, respectively, excess

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[1] The term "carbenium" (rather than the inveterate "carbonium" ion, which will be used in this paper, has been suggested by G. A. Olah [*J. Amer. Chem. Soc.*, **94**, 808 (1972)] for "classical" trivalent carbocations to differentiate them from "nonclassical" penta- or tetracoordinated carbocations.

[2] (a) This research resulted from an initial investigation included in the dissertation submitted by P. M. Cook to the Graduate School at Colorado School of Mines in partial fulfillment of the requirements for the M.S. degree, 1968; (b) presented in part at the1 61st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstracts, INORG 95.

[3] Although platinum tetrachloride has been reported from a powder X-ray diffraction study to possess the solid-state SnI_4 structure comprised of tetrahedral molecules,[4] we feel (in the absence to date of suitable single crystals for an X-ray crystallographic investigation) that our spectral data (presented below) provide conclusive evidence that this widely accepted possibility of such a simple monomeric species in the solid state can be definitely excluded. In addition (inasmuch as we cannot find such a suggestion in the literature), we propose that platinum tetrachloride has a cubane-like tetrameric structure both in the solid and vapor states and offer the following arguments to support our proposal. (a) No Pt(IV) complexes are known to possess tetrahedral coordination as proposed for platinum tetrachloride; furthermore, a crystalline arrangement of discrete $PtCl_4$ molecules would presumably give rise to a relatively volatile, paramagnetic complex which is not the case. Octahedral coordination can be achieved in $[PtCl_4]_x$ by chlorine bridge bonding either as in the known Pt(IV) cubane structures $[Pt(CH_3)_3Cl]_4$,[5] $[Pt(C_2H_5)_3Cl]_4$,[6] and $[PtCl(C_3H_6)Cl]_4$[7] or as in $[PtI_4]_\infty$[8] which contains an infinite zigzag chain of edge-linked $PtCl_6$ octahedra. The structure of PtX_3 (X = Cl, Br)[9] contains Pt(II) in $[Pt_6X_{12}]$ units and Pt(IV) in $[PtX_4]_\infty$ chains as in $[PtI_4]_\infty$. Our spectral data indicate that the cubane structure is more likely. (b) The far-infrared spectrum[10] of $[PtCl_4]_x$ shows absorption bands characteristic of both terminal and bridging chlorine atoms;[11] this spectrum is comparable to the spectra of $[Pt(CH_3)_3Cl]_4$ and $[PtCl(C_3H_6)Cl]_4$.[7]

	$\nu(Pt–Cl)_t$	$\delta(Pt–Cl)_t$	$\nu(Pt–Cl)_b$	$\delta(Pt–Cl)_b$
$[Pt(CH_3)_3Cl]_4$			220	140
$[PtCl(C_3H_3)Cl]_4$	330 d	180, 200	230	125
$[PtCl_4]_x$	337, 366, 376	182	275, 292	128

t = terminal chlorine, b = bridging chlorine, d = doublet

The large difference in the assigned platinum–bridging chlorine stretching frequencies can be readily rationalized by the strong trans influence of the terminal alkyl ligands in the two known cubane-like Pt(IV) compounds. The ability of a *trans*-methyl ligand to lower the Pt(IV)–Cl stretching frequency is illustrated in $PtCl_2(CH_3)_2\{P(CH_3)_2(C_6H_5)\}_2$ for which ν(Pt–Cl) is 332 cm^{-1} when the methyl groups are cis to the chlorine atoms and 242, 265 cm^{-1} when the methyl groups are trans to the chlorine atoms.[12] The same trans influence can be exerted on platinum–bridging chlorine stretching frequencies as in $Pt_2Cl_4\{P(C_6H_5)_3\}_2$ which has ν(Pt–Cl) equal to 320 cm^{-1} when the chlorine atoms are trans to each other but 260 cm^{-1} when the chlorine atom is trans to triphenylphosphine.[13] (c) The mass spectrum of $[PtCl_4]_x$ consists of a parent *m/e* peak centered at 1348 due to $[Pt_4Cl_{16}]^+$ and contains a rich fragmentation pattern completely consistent with a cubane structure. The only peaks found above the parent-ion peak are attributed to $[Pt_5Cl_{19}]^+$, $[Pt_5Cl_{18}]^+$, and $[Pt_5Cl_{17}]^+$ with only $[Pt_5Cl_{19}]^+$ having a high relative abundance; these three species are ascribed to a thermal rearrangement which is common for metal cluster systems. (d) Our X-ray powder film and powder diffractometry measurements of $[PtCl_4]_x$ samples prepared by the method of Keller[14] and also purchased from Alfa Inorganics, Inc., do not correspond to the powder patterns reported by Falqui.[4] Our patterns, which are all the same, cannot be indexed in the cubic crystal system. If $[PtCl_4]_x$ crystallizes into more than one crystal system, the cubic crystal form reported by Falqui[4] should have the cubane structure since her determined lattice length of a = 10.45 Å is nearly identical with that of a = 10.55 Å given[5] for $[Pt(CH_3)_3Cl]_4$ which also belongs to the cubic crystal system. Although the spatial requirement of a terminal methyl group about a platinum(IV) atom is almost exactly that of a terminal chlorine atom, a structure factor analysis of Falqui's powder diffraction data shows that crystalline $[PtCl_4]_x$ is not isomorphous with $[Pt(CH_3)_3Cl]_4$. A $[PtI_4]_\infty$ type of structure is impossible in her cubic unit cell.

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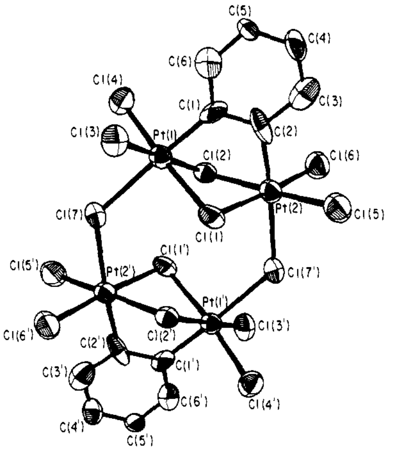

Figure 1. Architecture of the $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion which possesses crystallographic site symmetry C_i-$\bar{1}$; its geometry closely conforms to D_{2h}-$2/m2/m2/m$ symmetry. Important average distances within each of the two identical $[Pt_2(C_6H_4)Cl_6]$ moieties are Pt–Cl(terminal), 2.274 (4) Å; Pt–Cl (bridging), 2.352 (4) Å; Pt–C, 1.97 (2) Å; Pt (1)···Pt(2), 3.258 (2) Å. The Pt–Cl (bridging) bonds connecting the two $[Pt_2(C_6H_4)Cl_6]$ moieties average 2.533 (6) Å.

triphenylmethyl chloride in the reaction mixture does not appear to greatly affect the relative yield of each product.

Infrared spectra of **1–5** show the typical triphenylcarbenium ion spectrum[15] as well as absorption bands in the far-ir attributable to vibrational modes involving terminal and bridging chlorine ligands. Uv and ^1H nmr spectra also are typical of the triphenylcarbenium ion.[16] X-Ray structural investigations of the five isolated compounds were carried out[17,18] because a characterization of each anion by alternate methods was doubtful.

The anion of **1** is indeed monomeric with one chlorine of the CH_2Cl_2 molecule of crystallization occupying the sixth octahedral coordination site. Unfortunately, the crystal structure of **1** is disordered, and hence the positions of the uncoordinated chlorine of the CH_2Cl_2 molecule and the methylene carbon atom have not yet been unambiguously determined.

The dimeric $[Pt_2Cl_{10}]^{2-}$ anion of **2** expectedly consists of two edge-shared octahedra of chlorine atoms with the two Pt(IV) atoms thereby joined by two bridging chlorine atoms. The $[Pt_2Cl_{10}]^{2-}$ anion has an idealized D_{2h} geometry with the Pt–Cl(bridging) bonds of average length 2.374 (1) Å being significantly longer than the Pt–Cl(terminal) ones of average length 2.298 (1) Å. Other analogous $[M_2Cl_{10}]^n$ systems characterized by X-ray diffraction include the $[Ti_2Cl_{10}]^{2-}$ anion,[19] Nb_2Cl_{10},[20] Mo_2Cl_{10},[21] and Re_2Cl_{10}.[22]

The formation of **1** from the reaction of $[PtCl_4]_4$ with $(C_6H_5)_3CCl$ in CH_2Cl_2 is apparently followed by slow dimerization to **2**. The slow rate of reaction could be due to the ability of CH_2Cl_2 to strongly coordinate to the $[PtCl_5]^-$ anion, thus preserving octahedral coordination about the d^6 Pt(IV) as well as fulfilling the effective atomic number rule common to Pt(IV) compounds.

The $[Pt_3Cl_{12}]^{2-}$ anion of **3** has an idealized D_{2h} geometry which consists of three linearly arranged Pt atoms connected by chlorine-bridged bonds. Two terminal $[PtCl_6]$ octahedra are each edge shared by the central Pt atom through two di-μ-chloro linkages giving a square-planar geometry to the central Pt atom with a formal oxidation state of II instead of IV. The Pt(IV)–Cl(bridging) distances of average value 2.384 (3) Å are significantly longer than the Pt(II)–Cl (bridging) distances of average value 2.300 (3) Å. This anion could result from the initial formation of a similar linear, chlorine-bridged $[Pt_3Cl_{14}]^{2-}$ anion which subsequently loses the two axial chlorine atoms on the central Pt atom as Cl_2 thereby reducing the central Pt(IV) to the platinous (II) state. Such a reduction is reported to take place in the case of the long-known, unstable chlorine-bridged bis(tri-*n*-propylphosphine) complex, $Pt_2Cl_8(PPr_3)_2$, to give the stable $Pt_2Cl_4(PPr_3)_2$ dimer containing square-planar Pt(II) atoms linked by bridging chlorine atoms.[23] Numerous examples[24] of compounds with mixed metal valency exist, but Pt(II)–Pt(IV) compounds usually occur either as a mixture of separate Pt(II) and Pt(IV) units as found in $PtCl_3$[9] or as alternating Pt(II) and Pt(IV) species oriented in chains as occurs in $[Pt(en)_2Br_2][Pt(en)_2Br_4]$.[25]

$[PtCl_4]_4$ reacts completely with $(C_6H_5)_3CCl$ in 1,1,2,2-tetrachloroethane to give **4** as the only detectable product. The ir spectrum of the red crystals obtained by evaporation is the same as that of the reaction solution. An X-ray diffraction study showed that both the cation and anion of **4** are identical with those of **3** but that **4** crystallizes into a different space group due to an accompanying solvent molecule of crystallization. The nonisolation of the monomeric anion is under-

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(17) (a) $[(C_6H_5)_3C]^+[PtCl_5 \cdot CH_2Cl_2]^-$ (**1**): monoclinic, $P2_1/c$; a = 11.343 (3) Å, b = 14.498 (5) Å, c = 15.442 (3) Å, β = 111.96 (1)°; ρ_{obsd} = 1.96 g cm^{-3} *vs.* ρ_{calcd} = 1.98 g cm^{-3} for Z = 4. Least-squares refinement gave $R_1(F)$ = 8.4% and $R_2(F)$ = 9.2% for 743 independent diffractometry data ($I > 2\sigma(I)$). (b) $[(C_6H_5)_3C]^+{}_2[Pt_2Cl_{10}]^{2-}$ (**2**): triclinic, $P\bar{1}$; a = 10.152 (2) Å, b = 13.030 (3) Å, c = 18.197 (6) Å, α = 122.41 (1)°, β = 87.27 (2)°, γ = 100.39 (1)°; ρ_{obsd} = 2.06 g cm^{-3} *vs.* ρ_{calcd} = 2.05 g cm^{-3} for Z = 2. Least-squares refinement gave $R_1(F)$ = 3.3% and $R_2(F)$ = 4.7% for 2058 independent diffractometry data ($I > 2\sigma(I)$). (c) $[(C_6H_5)_3C]^+{}_2[Pt_3Cl_{12}]^{2-}$ (**3**): triclinic, $P\bar{1}$; a = 10.725 (2) Å, b = 12.645 (2) Å, c = 8.712 (2) Å, α = 95.34 (1)°, β = 98.98 (1)°, γ = 109.40 (1)°; ρ_{obsd} = 2.28 g cm^{-3} *vs.* ρ_{calcd} = 2.29 g cm^{-3} for Z = 1. Least-squares refinement gave $R_1(F)$ = 4.2% and $R_2(F)$ = 4.9% for 1550 independent diffractometry data ($I > 2\sigma(I)$). (d) $[(C_6H_5)_3C]^+{}_2[Pt_3Cl_{12}]^{2-} \cdot 2C_2H_2Cl_4$ (**4**): monoclinic, $P2_1/c$; a = 9.403 (2) Å, b = 29.645 (4) Å, c = 10.559 (2) Å, β = 105.99 (1)°; ρ_{obsd} = 2.14 g cm^{-3} *vs.* ρ_{calcd} = 2.15 g cm^{-3} for Z = 2. Least-squares refinement gave $R_1(F)$ = 6.3% and $R_2(F)$ = 8.5% for 1474 independent diffractometry data ($I > 2\sigma(I)$). (e) $[(C_6H_5)_3C]^+{}_2[Pt_4(C_6H_4)_2Cl_{14}]^{2-} \cdot 2CH_2Cl_2$ (**5**): monoclinic, $P2_1/c$; a = 12.173 (2) Å, b = 21.376 (7) Å, c = 12.400 (2) Å, β = 107.77 (1)°; ρ_{obsd} = 2.28 g cm^{-3} *vs.* ρ_{calcd} = 2.25 g cm^{-3} for Z = 2. Least-squares refinement yielded $R_1(F)$ = 4.5% and $R_2(F)$ = 5.2% for 1658 independent diffractometry data ($I > 2\sigma(I)$).

(18) For computation of distances and bond angles, atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-5511. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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standable from steric considerations; the greatly increased size of the 1,1,2,2-tetrachloroethane molecule should result in weaker coordination of the solvent molecule to a $[PtCl_5]^-$ group as a sixth octahedral-like ligand than in the case of methylene chloride and thus should facilitate polymerization. $[PtCl_4]_4$ will not react with $(C_6H_5)_3CCl$ in chloroform, 1,1,1-trichloroethane, *tert*-butyl chloride, or trichloroethylene. The bulkiness of these polar solvents presumably may prevent them from occupying the sixth coordination site to form a $[PtCl_5\cdot solvent]^-$ anion which can then polymerize.

Although reaction also does not occur in nonpolar cyclohexane, which has often been used to prepare triphenylcarbenium salts,[26] a reaction does occur in benzene to yield the red product **5**. A slurry of finely powdered $[PtCl_4]_4$ in benzene is mixed with $(C_6H_5)_3CCl$ in excess of a 1:1 mole ratio at ~50° for 24 hr or more. The resultant orange-red solid is filtered under N_2 and washed several times with dry hexane. The product can then be dissolved in CH_2Cl_2 and filtered to give a red solution. More than one product may be present, because much of the solid readily dissolves in CH_2Cl_2 leaving a smaller amount of less soluble yellow powder which exhibits a different far-infrared spectrum than **5**. Crystallization from CH_2Cl_2 gave crystals of **5** suitable for X-ray diffraction studies when hexane was slowly diffused into the concentrated CH_2Cl_2 solution. These crystals are hygroscopic but can be stored indefinitely in a desiccator. Due to the difficulty in obtaining crystals, the amount of pure product **5** isolated has not exceeded a 5% yield. An X-ray diffraction study of **5** revealed it to be a triphenylcarbenium salt of the highly unusual $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion (Figure 1). This tetranuclear Pt(IV) anion of idealized D_{2h} geometry consists of two $[Pt_2(C_6H_4)Cl_6]$ moieties linked to each other by two bridging chlorine atoms. Each $[Pt_2(C_6H_4)Cl_6]$ moiety is comprised of two $PtCl_2$ fragments joined by two di-μ-chloro linkages and one bridging *o*-phenylene ring. Each Pt(IV) of the $[Pt_2(C_6H_4)Cl_6]$ moiety completes its octahedral coordination sphere by dimerization through the remaining two bridging chlorine atoms to give the $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion. Preparation of other examples of a benzene ring σ bonded to more than one transition metal were reported recently.[27,28] The $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion provides the initial case of an X-ray determination of such a structure as well as the first Pt(IV)–phenyl compound.[29] The loss of two protons from each benzene to give an *o*-phenylene group was detected qualitatively by a bubbling of the N_2-flushed gas from the reaction flask through an $AgNO_3$ solution which precipitated the evolved HCl gas as AgCl. Clearly, a complex mechanism is involved in the formation of this product.

Detailed descriptions of the structures of these anions and the triphenylcarbenium cation as well as their chemical and physical characterization and reactions with small molecules will be reported upon completion of closely related work now in progress.

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An Unusually Large Conformational Kinetic Isotope Effect in [2.2]Metaparacyclophane

Sir:

Although zero-point vibrational energy differences are generally accepted as the origin of secondary deuterium isotope effects, a number of rationales for the necessary changes in vibrational force constants have been suggested. The relative significance of hyperconjugative, inductive, and steric factors in a given system often is unclear.[1] The steric factor, proposed by Bartell[2] and ascribed great generality by Brown, *et al.*,[3] has been isolated most strikingly in studies of conformational kinetic isotope effects.[4,5] We felt that 8-deuterio[2.2]metaparacyclophane (**1**-*d*) was an attractive subject for such a study. The free energy of activation for ring flipping in **1**-*H* had been measured as about 20 kcal/mol[6] and seemed likely to involve primarily nonbonding interaction between the 8 hydrogen and the π cloud of the para-bridged ring. The magnitude of this barrier and the rigidity and symmetry of **1** suggested that compression of the 8 carbon–hydrogen bond in the transition state probably exceeds that involved (per isotopic bond) in previously studied examples and should result in a larger isotope effect.

Oxidation of 9-bromo-2,11-dithia[3.3] metaparacyclophane[7] with metachloroperbenzoic acid gave nearly

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